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A Method for Determining Compatibility Parameters of Plasticizers for Use in PVC Through Use of Torsional Modulus

Measurements of torsional modulus of poly(vinyl chloride) plasticized with different types of plasticizers have shown various characteristics. One of these characteristics is the different maximum slopes obtained when torsional modulus is plotted with respect to temperature for the various plasticizers. It was believed that the slope obtained was associated with the compatibility or permanence of the plasticizer.

According to Webster (1) compatibility is "the capacity of two or more entities to combine or remain together without undesirable effects." In the plastics field compatibility means the ability of the plasticizer and the plastic to mix and remain homogeneously dispersed in one another. Frequently substances are found which appear to be miscible with the plastic but on standing, exudation occurs. This exudation reflects the permanence of the plasticizer. The volatility and migration in contact with another medium are also permanence properties and are effected by the compatibility. No external plasticizer is completely permanent as it can be removed without breakdown from the plastic by heat, light, solvent extraction and other means.

This paper explains how the relative degree of compatibility of mechanically dispersed plasticizers with poly(vinyl chloride) can be determined and how the relative degree of migration can be estimated by use of torsional modulus data.

Experimental

Materials—The materials used in this study were mainly compounds prepared for experimental testing as plasticizers of PVC. In addition several commercial plasticizers were included.

Plasticizer Evaluation—A three component formulation of resin, plasticizer and stabilizer was used. Various stabilizers were used as required to process the combined materials; however, the amounts were small enough that they did not effect the physical properties. Plasticizer and stabilizer comprised 35% of the total mix, PVC 65% (Geon 101). The formulations were milled at 160°C for 7 min. Samples were molded at 160°C in the manner previously reported (2). The molded samples were stored at room conditions of 23°C and 50% relative humidity.

It has become common practice to measure the stiffness in torsion as a function of temperature. This method was introduced by Clash and Berg (3) who arbitrarily selected an apparent modulus of elasticity of 135,000 psi as the borderline betwen a rigid and nonrigid material. This is a value called the flex temperature T_f. The temperature at which the stiffness of 10,000 psi is observed is called T_4 and is significant because of its equivalence to the temperature of maximum slope. The T_4 temperature is considered by some to be of more significance since it is approximately equivalent to the temperature at which the sample exhibits its maximum sensitivity to change of stiffness with temperature. This test only requires one small sample, 6.3 x .6 x approx. .15 cm.

Determination of tensile strength, 100% modulus, elongation, volatility and migration were obtained by previous reported methods (4).

Volatility values were obtained at 70°C and migration values with the sample in contact with silicic acid at 23°C. Exudation where noted in the discussion is that found at the above mentioned room conditions (no elevated temperature), with samples exposed to air in the presence of normal room lighting.

Discussion

From the data of an evaluation study of a series of brassylic acid diesters as plasticizers for PVC (4), there was found to be a relationship of the torsional modulus slope (T_f — T_4) with compatibility and permanence. Other physical property relationships were also found but will not be discussed here. To see whether this relationship was true for other plasticizers, a check was made of the most commonly used plasticizers and the same relationship was found.

Compatibility Number—Shown in *Figure 1* is the curve obtained from the plot of torsional modulus versus temperature for PVC plasticized with 35% DOP (di-2-ethylhexylphthalate). The difference between T_f and T_4 indicates the degree of compatibility and permanence of the plasticizer. This difference as used in this paper is designated as Δ, the compatibility number. The smaller the number is, the more compatible is the plasticizer; the larger the number, the less compatible or most likely to exudate. As used here permanence refers to migration of the plasticizer; however, it is recognized that volatility will also effect the permanence and must be taken into account in the final overall analysis of permanence. Concerning volatility, it has been stated that a plasticizer should have a boiling point above 200°C at a pressure of 4 mm of mercury to have sufficient permanence for most applications (5). Naturally if the plasticizer does not meet this criteria, it will have poor permanence through volatility in addition to migration.

When the T_f values of the five plasticizers of *Table I* are plotted against their compatibility number Δ, a straight line is obtained (*Figure 2*), fitted best by the data for TCP, DOP and DOZ. These plasticizers were chosen arbitrarily as standards since they exhibit good compatibility at their respective T_f temperature. The straight line plot is then taken as a graphical standard for estimating the compatibility of other plasticizers with respect to these commonly used plasticizers.

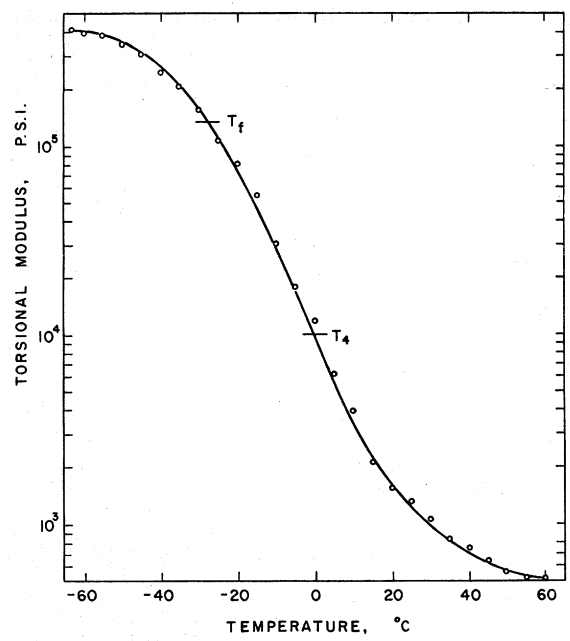

Figure 1. Typical torsional modulus versus temperature curve for PVC plasticized with 35% DOP.

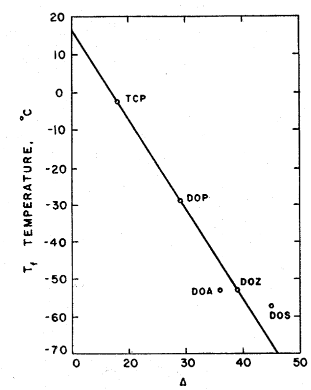

Figure 2. Plot of stiffness temperature (T_f) versus compatibility number (Δ) for plasticized PVC used to select a standard compatibility line.

Table I. Physical Properties of Plasticized PVC Sheets

Commercial Plasticizers	Torsional Stiffness Temp. °C T_f	Torsional Stiffness Temp. °C T_4	Compatibility Number Δ	Permanence: Migration Wt. Loss %	Permanence: Volatility Wt. Loss %	Tensile Strength PSI	Elongation %	100% Modulus PSI
TCP	—2	16	18	0.5	0.3	3000	255	1900
DOP	—29	0	29	6.0	1.7	2700	325	1150
DOZ	—53	—14	39	18.3	1.6	2400	340	960
DOA	—53	—17	36	17.6	3.4	2400	340	890
DOS	—57	—12	45	19.1	2.5	2400	340	970

Table II. Physical Properties of Plasticized PVC Sheets

Brassylic Acid Diesters	Torsional Stiffness Temp. °C T_f	T_4	Compatibility Number Δ	Permanence: Migration Wt. Loss %	Permanence: Volatility Wt. Loss %	Tensile Strength PSI	Elongation %	100% Modulus PSI
Methyl	—45	—14	31	19.0	23.0	2450	430	630
Ethyl	—50	—16	34	18.3	14.0	2450	320	700
Propyl	—53	—16	37	21.1	5.8	2300	330	710
Butyl	—55	—18	37	22.1	3.2	2300	350	740
2-Ethylbutyl	—53	—14	39	18.7	1.4	2450	380	990
Hexyl	—51	0	51	22.6	1.4	2300	380	860
Di-2-Ethylhexyl	—63	1	64	19.7[a]	4.1[a]	2250	320	1120
Cyclohexyl	—29	—2	27	5.8	0.8	2500	370	1000

[a] Sample showed exudate after 48 hours.

The straight line plot shows that as the T_f temperature is lowered the compatibility number becomes larger and the lower the T_f temperature, the greater the migration of the plasticizer which is shown in *Table I*. The plasticizer migration can therefore be predicted by this method as it relates to the low temperature stiffness.

A plasticizer with a compatibility number plotted above (to the right of) the line will be less compatible than the standard and, conversely, a plasticizer plotted below (to the left of) the line will be more compatible than the arbitrary standards. This line is then used as the standard for different groups of compounds having similar T_f temperature properties.

Experimental Data—The properties of several brassylic acid esters which have been investigated as plasticizers for PVC (4) are listed in Table II. With the exception of the cyclohexyl ester, all are low temperature plasticizers with high migration values. As should be expected, the volatility is noted to decrease as the chain length increases.

The plot of the compatibility values for these esters is shown in *Figure 3*. The cyclohexyl, methyl, ethyl, propyl and butyl ester values lie to the left of the line and the 2-ethylbutyl on the line which indicates good compatibility. On the other hand, the hexyl and di-2-ethylhexyl esters show poor compatibility, being located to the right of the standard line. The di-2-ethylhexyl ester value shows very poor compatibility with respect to the line. This is corroborated by observation of surface exudate after 48 hours at room conditions. The 2-ethylbutyl value occupies the same plotted position as DOZ and both have nearly the same migration and volatility values with no exudation observed after two years for either sample.

Table III shows some of the physical properties of 4 diesters of α-sulphopalmitic acid. These esters have low volatilities and moderate migration values.

The plotted compatibility numbers of these esters (*Figure 4*) are found to lie to the right of the standard line. The dioctyl ester showed surface exudate after three days, the dihexyl after one month, and the diethyl after slightly more than two months. The dibutyl which according to its position with respect to the line appears to have the greatest compatibility showed exudate after six months. The data indicates for numbers located to the right that the proximity of the plotted number to the standard line indicates the relative time for exudation to appear at room temperature.

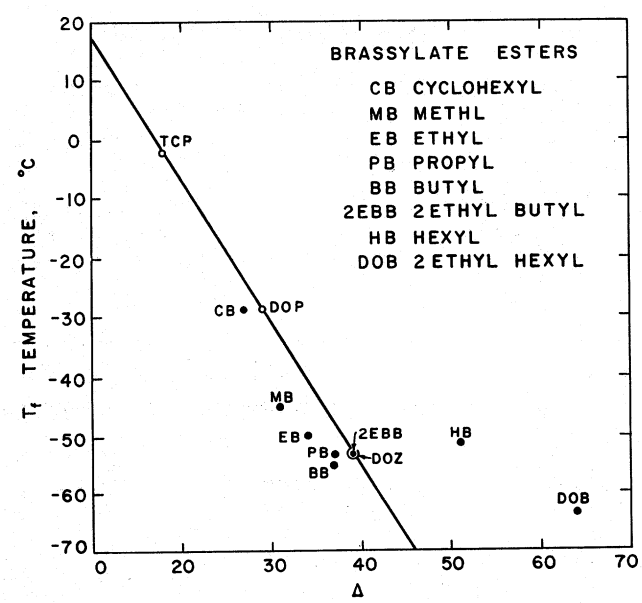

Figure 3. Compatibility of plasticizers with PVC compared to standard line.

Table III. Physical Properties of Plasticized PVC Sheets

α Sulpho-palmitic Acid Diesters	Torsional Stiffness Temp. °C T_f	T_4	Compatibility Number Δ	Permanence: Migration Wt. Loss %	Permanence: Volatility Wt. Loss %	Tensile Strength PSI	Elongation %	100% Modulus PSI
Ethyl	—29	9	38	13	1.4	2600	240	1300
Butyl	—37	—2	35	13	0.7	2550	230	1375
Hexyl	—37	8	45	14	0.9	2450	220	1450
Octyl	—45	22	67	16[a]	4.0[a]	2250	280	1325

[a] Sample showed exudate after 3 days.

Table IV. Physical Properties of Plasticized PVC Sheets

Bis(3 dialkylesters of phosphonopropyl) Sebacate	Torsional Stiffness Temp. °C T_f	T_4	Compatibility Number Δ	Permanence: Migration Wt. Loss %	Permanence: Volatility Wt. Loss %	Tensile Strength PSI	Elongation %	100% Modulus PSI
Methyl	10	55	45	a	a	3300	280	2600
Ethyl	—20	14	34	1.2	4.0	3100	330	1800
Butyl	—22	9	31	1.3	3.0	2900	370	1600
2-Ethylhexyl	—26	8	34	0.9	1.0	2700	300	1400

[a] Sample showed exudate after 4 days.

Another group of compounds investigated as possible plasticizers were bis(3 dialkyl esters of phosphonopropyl) sebacate whose properties are shown in Table IV. These esters have moderate volatility and unexpectedly the migration values are lower than the volatility values. This is the reverse of what is usually found. The compatibility plot is shown in *Figure 5*. The sample containing the dimethyl ester had exudate on the surface after about four days at room condition. The diethyl sample had heavy surface exudate after two months. No exudate was noted for the dibutyl or di-2-ethylhexyl specimens after four months.

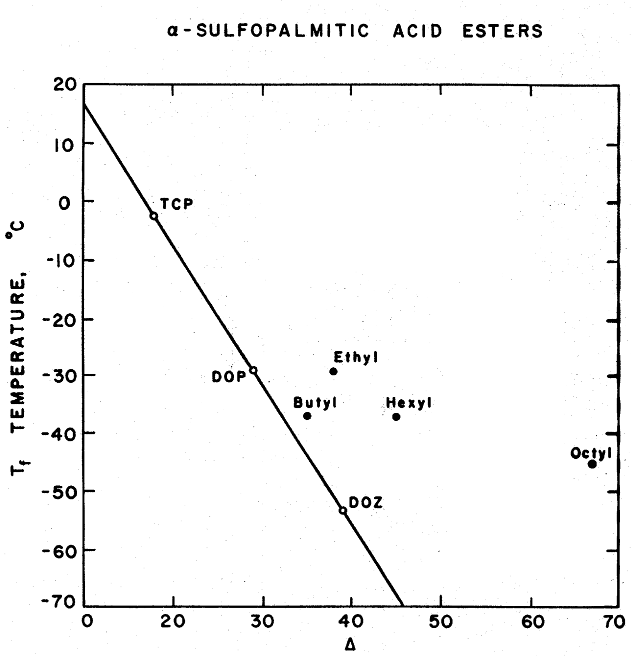

Figure 4. Compatibility of plasticizers with PVC compared to standard line.

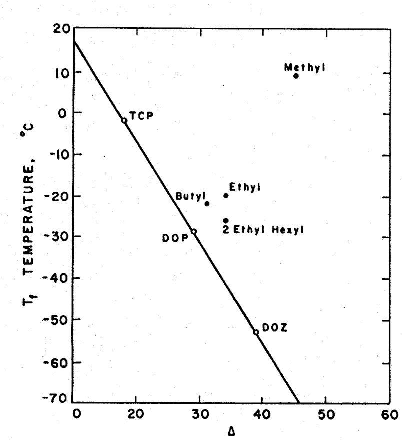

Figure 5. Compatibility of plasticizers with PVC compared to standard line.

Table V. Physical Properties of Plasticized PVC Sheets

Triglycerides	Torsional Stiffness Temp. °C T_f	T_4	Compatibility Number Δ	Permanence Migration Wt. Loss %	Volatility Wt. Loss %	Tensile Strength PSI	Elongation %	100% Modulus PSI
Triacetin	—24	3	27	>3.8[a]	>12.3	2700	250	1300
Tripropionin	—36	—8	28	10.9	19.4	2700	270	830
Tributyrin	—41	—13	28	13.7	20.0	2500	350	720
Tri-iso-valerin	—30	0	30	8.3	14.9	2600	270	1050
Trivalerin	—37	7	44	10.0	14.0	2600	350	1200
Trihexanoin (A)	—45	—2	43	20.9	10.0	2600	350	1050
Trihexanoin (B)	—43	—10	33	16.1	4.8	2650	320	900
Triheptanoin	—45	—10	35	17.3	1.5	2400	275	1000
Trioctanoin	—50	0	50	16.0	2.0	2550	360	1160
Tripelargonin	—49	16	65	14.1[a]	8.4[b]	2600	340	1400

[a] High plasticizer loss in processing.

[b] Sample showed exudate after 24 hours.

Several of the common triglycerides were studied to determine their plasticizing behavior with PVC. The observed data is given in Table V.

The triglycerides investigated produce low temperature properties below that found for DOP as noted by the T_f temperatures; however, these materials have volatilities that are much too high for good long-time permanence.

The plotted compatibility numbers are shown in *Figure 6*. The triacetin, even though its value falls on the line, was too volatile for processing to obtain accurate measurements. The sample became rigid after two years of storage at room condition. The tripropionin sample whose value shows excellent compatibility was found to be semirigid after two years. The tributyrin, even though it had a high volatility value, had good flexibility and no surface exudate after four years. The tri-iso-valerin also had good flexibility and no surface exudate after four years. The trivalerin, number 5, shows poor compatibility which was unexpected. From this, it was concluded that the triglyceride contained an impurity. In addition, the molded sample was observed to have lost some of its flexibility after four years. In a like manner, a trihexanoin sample (number 6A), whose compatibility number is located to the right of the line indicating poor compatibility, had a migration value which did not fit the apparent trend for the triglyceride series. A sample (number 6B) from another source showed good compatibility; in addition to showing a decrease in the migration value (20.9 to 16.1), the volatility number was greatly reduced (10.0 to 4.8). The triheptanoin (number 7) showing good compatibility with respect to the standard line, had not shown signs of surface exudate after fourteen months. The trioctanoin had light exudate on the sample surface after about two years. The tripelargonin, located on the plot the furthest from the line showed exudate after twenty-four hours.

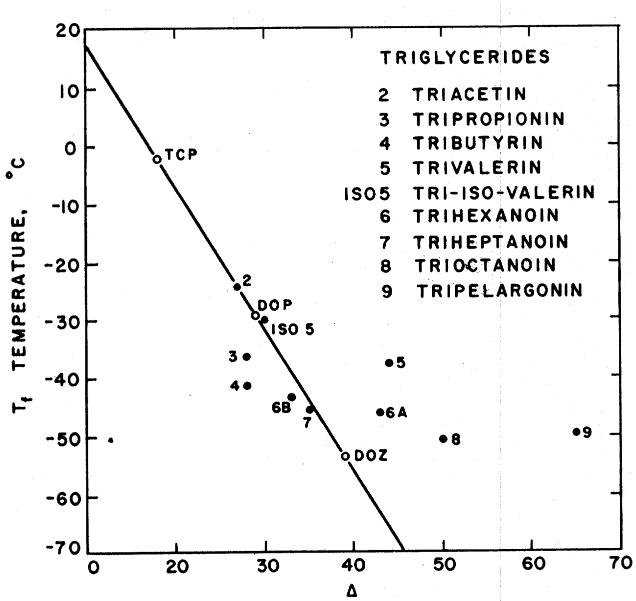

Figure 6. Compatibility of plasticizers with PVC compared to standard line.

Summary

A method to predict the compatibility of plasticizers with PVC has been shown. This method using torsional modulus is fairly rapid and requires only a single small sample. By comparing the difference in the T_f and T_4 temperatures obtained from torsional stiffness tests and plotting this difference with respect to an arbitrary standard, the degree of compatibility can be determined. The plotted data of this method also predicts the rate of migration that can be expected for the individual plasticizer. In addition improper compounding and plasticizer purity can be detected.

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